

Relativistic All-Electron Dirac–Fock–Breit Calculations on Xenon Fluorides (XeF_n , $n = 1, 2, 4, 6$)

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ABSTRACT

The MOLFDIR package of programs is used to perform fully relativistic all-electron Dirac–Fock and Dirac–Fock–Breit calculations for the XeF_n ($n = 1, 2, 4, 6$) molecules assuming experimental symmetries. The Xe–F bond length for XeF_2 , XeF_4 , and XeF_6 is optimized and the total ground-state energies are reported. The variation of the relativistic energy and the Breit correction with the internuclear distance is plotted. The role of relativistic corrections in the proper prediction of the Xe–F distance and the dissociation energy of the molecule is discussed. The problem of the reduction of the number of scalar two-electron integrals is studied. Our results illustrate the possibilities, difficulties, and limitations of the finite basis Dirac–Fock calculations for polyatomic molecules of different symmetries. © 1997 by John Wiley & Sons, Inc.

Introduction

Computational studies within a nonrelativistic model of systems that contain heavy atoms become inadequate: the high nuclear charges are

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the source of strong potentials due to which the innermost electrons possess energies that are no longer small compared to their rest mass energy mc^2 . In such a situation a better description can be obtained by using a relativistic method in predicting the electronic structure of a many-electron system.¹ Many different methods have been developed that allow the inclusion of relativistic effects in many-electron systems: relativistic perturbation theory, relativistic effective core potential, relativistic local density method, etc. The relativistic

analog of the Hartree–Fock (HF) method, the numerical Dirac–Fock (DF) method, was developed with great success for atoms by Desclaux² and Grant et al.³ In this approach, the one-electron Dirac equation is extended to a many-electron system by assuming the Hamiltonian for a system as a sum of one-electron Dirac Hamiltonians and Coulomb electron–electron interaction operators. The algebraic version of the DF method had already been proposed in 1975 by Malli and Oreg,⁴ but their implementation was limited by the technical possibilities of computers available two decades ago, because four-component relativistic DF calculations require much larger computer resources than the corresponding nonrelativistic HF ones. Progress in computational techniques in the 1980s and the introduction of the so-called “kinetic-balance” relation⁵ for the basis set expansion of large and small components of molecular spinors, accelerated the development of the algebraic version of the DF self-consistent field (SCF) method for molecules. During the last few years a number of DF programs for molecular systems have been derived and the results published.^{6–10}

Molecules containing noble gas atoms pose fascinating chemical problems, because their existence contravenes previously established ideas associated with the chemical inactivity of rare gases. Among these compounds, xenon fluorides seem particularly interesting.^{11–13} Various attempts have been made to understand theoretically the electronic structure of XeF_{*n*} (*n* = 1, 2, 4, 6).^{14–24} These have mostly utilized the conventional HF molecular orbital (MO) approach and in a few cases electron correlation effects have been included.^{14, 19, 24} However, the relativistic effects have been ignored, although one might expect them to be significant due to the high nuclear charge of Xe (*Z* = 54). The spectra of xenon fluorides were studied by different techniques.^{25–27} In the current article we present all-electron relativistic DF and DF–Breit (DFB) calculations for the series of XeF, XeF₂, XeF₄, and XeF₆ molecules. The importance of relativistic effects on the structure of these molecules is discussed. The role of relativistic effects on the prediction of the Xe–F bond length and the dissociation energy is presented.

DFB Method for Molecules

The detailed description of the relativistic many-electron DFB theory can be found in many

articles,^{4, 10, 28, 29} so we shall give only a brief description of this method.

The relativistic eigenvalue problem for a molecular system can be formulated as:

$$\sum_i \begin{bmatrix} V_i \cdot \mathbf{I}_2 & c(\boldsymbol{\sigma}_i \cdot \mathbf{p}_i) \\ c(\boldsymbol{\sigma}_i \cdot \mathbf{p}) & (V_i - 2mc^2)\mathbf{I}_2 \end{bmatrix} \Psi + \sum_{i < j} g(i, j)\Psi = E\Psi, \quad (1)$$

where \mathbf{I}_2 and $\boldsymbol{\sigma}$ are 2×2 identity and Pauli matrices, respectively; $V_i(\mathbf{r}; \mathbf{R})$ is the nuclear potential at \mathbf{r} (\mathbf{r} is the position vector of the electron, \mathbf{R} stands for the position vectors of the nucleus); c is the speed of light in vacuum; m is the rest mass of the electron; and \mathbf{p} is the electron momentum vector. The electron–electron interaction consists of the Coulomb operator and a relativistic correction to this interaction, the Breit interaction:

$$g(i, j) = \frac{\mathbf{I}_4}{r_{ij}} + B^{\text{mag}}(i, j) + B^{\text{ret}}(i, j), \quad (2)$$

where \mathbf{I}_4 is 4×4 identity matrix.

The magnetic part B^{mag} of the Breit interaction is dominant³⁰ (about one order larger than retardation part B^{ret}) and can be expressed by the so-called Gaunt operator:

$$B^{\text{mag}}(i, j) = -\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}}, \quad (3)$$

where $\boldsymbol{\alpha}_i$ is the 4×4 Dirac matrix of electron *i*. When the Breit interaction is omitted in eq. (1), one can derive the so-called DF–Coulomb equations. The many-electron wave function is then chosen as a Slater determinant built from four-component one-electron spinors. It is convenient to write these spinors in terms of two bispinors:

$$\begin{pmatrix} \Phi^L \\ \Phi^S \end{pmatrix}, \quad (4)$$

where Φ^L and Φ^S are the so-called large and small components of a molecular four-component spinor. The large and small component can be related by the so-called “kinetic balance” relation,^{5, 10} which ensures the proper convergence to the nonrelativistic limit upon increasing the value of *c*:

$$\Phi^S \approx -\frac{1}{2mc} \boldsymbol{\sigma} \cdot \mathbf{p} \Phi^L. \quad (5)$$

If we apply this relation to the primitive basis sets used to expand Φ^L and Φ^S , we can avoid the spurious solutions of the eigenvalue problem. In the molecular calculations, where atomic solutions are used to contract the large and small component basis functions, in addition to the kinetically balanced functions the atomic small component solutions are used as small component basis functions. Such a basis set is called a *kinetically and atomically balanced* basis set.³¹

In the relativistic basis set expansion calculations for a molecular system, it is convenient to use a potential of electron–nuclear interaction that corresponds to a Gaussian nuclear charge distribution of the nucleus³²:

$$\varphi = \rho_0 \exp[-\alpha(\mathbf{r} - \mathbf{R})^2], \quad (6)$$

where ρ_0 and α are parameters describing the nucleus. Such a potential removes the singularity associated with the point-nucleus potential and leads to simple formulas for the nuclear attraction integrals.

By minimizing the average of configuration energy expression (in a similar way as in the nonrelativistic case), one can obtain the open-shell DF equations.¹⁰ The solution of these equations gives the average energy, while the energies of individual states can be obtained by complete open-shell configuration interaction (COSCI),³³ i.e., the diagonalization of the CI matrix of all configurations in the open-shell manifold.

Calculations

BASIS SET

It was shown for a series of atoms that the results obtained in the DF SCF calculations using the universal Gaussian basis set (UGBS) are as accurate as those obtained in the numerical DF method.³⁴ The generation of UGBS allows one to obtain in a natural way the necessary high “relativistic” exponents. The disadvantage of the UGBS is that its size is larger than the size of an optimized atomic basis. However, the exponents of the UGBS for orbitals with different symmetry (different l) are subsets of the same set and this property allows a significant reduction of the small component basis set size, when the kinetic balance condition is used.

In our relativistic calculations for XeF_n ($n = 1, 2, 4, 6$), we used the UGBS of 27s23p13d func-

tions (with the mesh of 0.13) for the large component wave functions of the Xe atom. The kinetic balance condition¹⁰ was used to determine the basis set for the small component, i.e., 23s27p23d13f. This basis set was contracted to [L:6s9p5d|S:11s13p12d8f] using the general contraction scheme with the “atomic balance” procedure.³¹ Similarly, the uncontracted and contracted basis set for fluorine was L:18s12p|S:12s18p12d and [L:3s2p|S:3s4p4d], respectively. The exponents of the UGBS set for Xe and F are reported in our previous article.^{23a} For comparison with the nonrelativistic results, we also formed a nonrelativistic basis set using the same primitive exponents and the same contraction scheme. The resulting size of the nonrelativistic basis set for Xe and F is [6s5p3d] and [3s2p] respectively. The above described contracted basis sets were used in the relativistic investigation of XeF_n. These basis sets are valence double zeta in character; the extra functions in the relativistic large component are required to describe the spin-orbit splitting of the inner shells.

ATOMIC AND MOLECULAR CALCULATIONS

The DF calculations were performed on the ground-state electronic configuration of Xe, F, F₂, and the XeF_n ($n = 1, 2, 4, 6$) molecules, using the relativistic MOLDIR program.¹⁰ This program exploits the double-group symmetry to block diagonalize the Hamiltonian matrix (we will denote double groups by adding * to a symmetry group symbol). All calculations were performed assuming the experimental geometry, except for XeF₆ where we assumed O_h^* symmetry. In this molecule the geometry is slightly distorted from octahedral symmetry due to the “pseudo Jahn–Teller” effect.²⁶ Recent CISD + Q calculations by Crawford et al.²⁴ give the energy of the C_{3v} structure of XeF₆ at 0.99 eV below the energy of the O_h structure. However, because we are mainly interested in the importance of the relativistic corrections, the use of the octahedral approximation is considered justified. The atomic calculations for Xe and F were performed in O_h^* symmetry. For F₂ and XeF the calculations were performed in D_{4h}^* and C_{4v}^* symmetry, respectively. In the DF step we optimized the weighted average energy expressions arising from all $(2p_{1/2}2p_{3/2})^5$ and $(e_1e_2)^3$ configurations for F and XeF, respectively. These average energy DF calculations were followed by COSCI calculations, giving the energy of the ground state $^2P_{3/2}$ and $\Omega = 1/2$ for F and XeF, respectively.

The DF calculations for XeF_2 , XeF_4 , and XeF_6 were carried out assuming D_{4h}^* , D_{4h}^* , and O_h^* symmetry, respectively.

To optimize the bond length in these molecules, relativistic calculations were performed at four Xe–F distances: 1.85, 2.00, 2.15, and 2.30 Å for XeF and XeF_2 ; 1.80, 1.90, 2.00, and 2.10 Å for XeF_4 and XeF_6 . The potential energy values for the F_2 molecule were calculated at seven F–F distances. We also calculated the nonrelativistic energies at these distances using the same relativistic program and the Gaussian nuclear model. This enabled us to obtain in a consistent way the values of the DF relativistic corrections $\Delta E_{\text{rel}}^{\text{DF}}$ to the total energy of the molecules, defined as the difference between the DF energy E^{DF} and the nonrelativistic energy $E^{\text{nr}}(\text{Gn})$. In our DF calculations the electron–electron interaction was represented by the coulomb operator. The relativistic correction ΔE^{Br} to this interaction was taken into account, using perturbation theory with the dominant part of the Breit interaction, the Gaunt interaction $B^{\text{mag}}(i, j)$, as the perturbation and the DF wave function as the zero-order wave function.

TWO-ELECTRON INTEGRALS

The original version of the RELTWEL program calculates the two-electron integrals over the group of primitive functions and then transforms them to integrals over the general contracted functions.¹⁰ Such an algorithm gives the possibility of efficient vectorization of the code. To make calculations on our workstation computer (IBM RS 530/6000, SGI Challenge) feasible, this vectorized code was modified by the introduction of prescreening³⁵ in which the magnitude of an integral is estimated and compared to the specified threshold ε before evaluation. Only those integrals that are larger than ε are calculated exactly. This modification of the program slows down the process of integral calculations but significantly reduces the size of RAM required for the calculations. The two-electron integrals are calculated in four groups: $(LL|LL)$, $(SS|LL)$, $(SS|SS)$, and $(SL|SL)$. Only one representative of a set of integrals related by a symmetry operation is calculated. The number of integrals that have to be stored on a disk can be further reduced by specifying higher (10^{-12} by default) thresholds separately for each of these groups ($\varepsilon^{LL|LL}$, $\varepsilon^{SS|LL}$, $\varepsilon^{SS|SS}$, $\varepsilon^{SL|SL}$). The values of these thresholds, however, need to be chosen with care. As a result of the kinetic balance condition (5), we

can assume that $(SS|LL)$, $(SL|SL)$, and $(SS|SS)$ integrals will give a contribution to the Fock matrix that is of the order $1/2c^2$, $1/2c^2$, and $1/2c^4$ times smaller respectively, than the contribution from the $(LL|LL)$ integrals. Corresponding relations can be used in defining the magnitudes of the integral thresholds. In our atomic and molecular calculations we tried various thresholds for $(LL|LL)$ at 10^{-12} – 10^{-10} , $(SS|LL)$ and $(SL|SL)$ at 10^{-12} – 10^{-7} , and $(SS|SS)$ at 10^{-12} – 10^{-3} . We found that even with a threshold of 10^{-3} for the $(SS|SS)$ integrals, the total energy is essentially the same as that obtained using the threshold of 10^{-12} . In Table I the role of symmetry and thresholds in the reduction of the number of two-electron integrals, which are to be stored on a disk, is shown. In this table the total number of integrals (TOT), the number of symmetry-unique nonzero integrals (NZ), and the number of integrals, whose value is greater than the specified threshold (AT), are given for each group of integrals for XeF_n ($n = 1, 2, 4, 6$). One can see that the reduction of the number of integrals resulting from exploiting the symmetry is crucial: the number of integrals is approximately decreased by factors of 7, 14, 15, and 45 for XeF , XeF_2 , XeF_4 and XeF_6 , respectively. The use of the “threshold method” is also efficient, for example the number of $(SS|SS)$ integrals is further reduced by a significant factor (1.7–3) for these molecules. However, one has to keep in mind that the kinetic balance relation is exact only for free electrons and care is always necessary when the value of the threshold is chosen for a given group of integrals.

Results and Discussion

The results of our nonrelativistic and relativistic calculations for the Xe and F atoms and the F_2 molecule are presented in Table II. The DF SCF total energies obtained with our contracted relativistic UGBS for the Xe and F atoms are -7446.8357 and -99.5013 au, respectively. The DF SCF COSCI energy of the ground state (2P) of F is -99.5020 au. The corresponding values of the DF SCF energies obtained using the finite-difference DF computer code^{3b} are -7446.8469 and -99.5023 au, respectively. The nonrelativistic total energies $E^{\text{nr}}(\text{Gn})$ are also given in this table. In the last two columns the ground state energy (E_{min}) of F_2 and the corresponding F–F distance (R_{min}), determined by fitting the calculated potential energy values to a fourth-order polynomial, are given.

TABLE I.

Number of Integrals for XeF_n (*n* = 1, 2, 4, 6) Molecules at Xe – F Internuclear Distance *R* = 2.00 Å.

Types of Integrals		XeF <i>C</i> _{4<i>v</i>} [*]	XeF ₂ <i>D</i> _{4<i>h</i>} [*]	XeF ₄ <i>D</i> _{4<i>h</i>} [*]	XeF ₆ <i>O</i> _{<i>h</i>} [*]
LL LL	TOT	3,454,506	5,516,181	122,537,25	23,829,156
	NZ	497,183	411,925	844,463	572,165
	AT	358,021	408,098	830,691	559,855
SS LL	TOT	76,635,108	130,648,140	318,091,950	657,621,198
	NZ	10,393,531	9,016,684	20,962,537	14,707,205
	AT	7,367,661	8,445,019	18,814,522	12,880,225
SS SS	TOT	425,196,541	773,837,470	2,064,770,191	4,537,853,011
	NZ	55,816,999	51,247,813	132,871,283	98,074,010
	AT	31,904,772	19,133,744	77,069,640	32,648,632
SL SL	TOT	150,554,628	257,202,540	628,085,403	1,301,137,578
	NZ	20,277,715	17,576,912	41,090,618	28,826,424
	AT	13,720,149	14,024,904	36,845,791	19,141,868

TOT is the total number of integrals. NZ is the number of symmetry-unique nonzero integrals. AT is the number of NZ integrals above the specified threshold; we used the following thresholds in our calculations:

	LL LL	SS LL	SS SS	SL SL
XeF	10 ^{−10}	10 ^{−08}	10 ^{−06}	10 ^{−07}
XeF ₂	10 ^{−10}	10 ^{−08}	10 ^{−04}	10 ^{−06}
XeF ₄	10 ^{−10}	10 ^{−08}	10 ^{−06}	10 ^{−08}
XeF ₆	10 ^{−10}	10 ^{−08}	10 ^{−05}	10 ^{−06}

The relativistic DF energies E^{DF} and the nonrelativistic HF energies $E^{\text{nrel}}(\text{Gn})$ at various internuclear distances Xe–F for XeF_n (*n* = 1, 2, 4, 6) are displayed in Table III. The relativistic correction to the Coulomb interaction, the Gaunt correction, is also given in this table. The variation of these energies with internuclear distance for XeF, XeF₂, XeF₄ and XeF₆ is shown in Figures 1–3. The Gaunt correction is almost independent of the Xe–F distance as indicated in Figure 3. This is due to the

fact that the valence contribution to this term is very small. The correction mainly affects the interaction between the core electrons, which is not very sensitive to changes in the Xe–F distance. It can be seen from Figures 1 and 2 that the potential energy curves obtained in the nonrelativistic and relativistic calculations for the ground state of XeF are repulsive. This result agrees with the conclusions from earlier studies on xenon monofluoride^{14,15} that this molecule can be expected to be

TABLE II.

Relativistic Dirac – Fock, Breit, and Nonrelativistic Energies (in au) for F, Xe, and F₂.

Energy	<i>E</i> (Xe)	<i>E</i> (F)	<i>E</i> _{min} (F ₂)	<i>R</i> _{min} (F ₂)
$E_{\text{av}}^{\text{nrel}}(\text{Gn})$		−99.409120		
$E^{\text{nrel}}(\text{Gn})$	−7232.005367	−99.409120	−198.742343	1.3178 Å
$E_{\text{av}}^{\text{DF}}$		−99.501292		
E^{DF}	−7446.835654	−99.501961	−198.926497	1.3176 Å
ΔE^{Br}	6.440639	0.011925	0.023906	
$E_{\text{av}}^{\text{DF}} + \Delta E^{\text{Br}}$	−7440.395015	−99.489367	−198.902591	1.3179 Å

Energies obtained using a Gaussian nuclear model, with the exponents 150202323.3 and 544953472.0 for Xe and F, respectively. For F₂ the minimum value (*E*_{min}) of the energy and the corresponding Xe–F distance (*R*_{min}) obtained by the polynomial fitting of the calculated potential energy values are given.

$E_{\text{av}}^{\text{nrel}}(\text{Gn})$ is the nonrelativistic average energy; $E^{\text{nrel}}(\text{Gn})$ is the nonrelativistic ground state energy; $E_{\text{av}}^{\text{DF}}$ is the Dirac–Fock average energy; E^{DF} is the Dirac–Fock ground state energy; and ΔE^{Br} is the Gaunt correction.

TABLE III.
Relativistic Dirac – Fock, Breit, and Nonrelativistic Energies (in au) for XeF_n (n = 1, 2, 4, 6) at Various Internuclear Distances R (in Å).

Energy ¹	R = 1.85	R = 2.00	R = 2.15	R = 2.30
XeF				
$E_{av}^{nrel}(Gn)$	– 7331.202773	– 7331.276177	– 7331.326308	– 7331.359085
$E^{nrel}(Gn)$	– 7331.270403	– 7331.319400	– 7331.353701	– 7331.376345
E_{av}^{DF}	– 7546.130828	– 7546.203738	– 7546.252784	– 7546.284490
E^{DF}	– 7546.194810	– 7546.244448	– 7546.278411	– 7546.300479
ΔE^{Br}	6.452878	6.452827	6.452778	6.452728
$E_{av}^{DF} + \Delta E^{Br}$	– 7539.678000	– 7539.750911	– 7539.800006	– 7539.831762
XeF ₂				
$E^{nrel}(Gn)$	– 7430.698413	– 7430.719544	– 7430.703581	– 7430.671835
E^{DF}	– 7645.711634	– 7645.735308	– 7645.720847	– 7645.689813
ΔE^{Br}	6.464365	6.464226	6.464154	6.464121
$E^{DF} + \Delta E^{Br}$	– 7639.247269	– 7639.271082	– 7639.256693	– 7639.225692
XeF ₄				
$E^{nrel}(Gn)$	– 7629.325952	– 7629.384220	– 7629.390943	– 7629.367180
E^{DF}	– 7844.522582	– 7844.583665	– 7844.592067	– 7844.569037
ΔE^{Br}	6.487988	6.487754	6.487608	6.487526
$E^{DF} + \Delta E^{Br}$	– 7838.034594	– 7838.095911	– 7838.104459	– 7838.081511
XeF ₆				
$E^{nrel}(Gn)$	– 7827.908950	– 7828.010933	– 7828.024817	– 7827.988714
E^{DF}	– 8043.309653	– 8043.404857	– 8043.414155	– 8043.374896
ΔE^{Br}	6.511538	6.511115	6.510885	6.510788
$E^{DF} + \Delta E^{Br}$	– 8036.798115	– 8036.893742	– 8036.903270	– 8036.864108
XeF ₂				
	R = 1.80	R = 1.90	R = 2.00	R = 2.10
XeF ₄				
$E^{nrel}(Gn)$	– 7629.325952	– 7629.384220	– 7629.390943	– 7629.367180
E^{DF}	– 7844.522582	– 7844.583665	– 7844.592067	– 7844.569037
ΔE^{Br}	6.487988	6.487754	6.487608	6.487526
$E^{DF} + \Delta E^{Br}$	– 7838.034594	– 7838.095911	– 7838.104459	– 7838.081511
XeF ₆				
$E^{nrel}(Gn)$	– 7827.908950	– 7828.010933	– 7828.024817	– 7827.988714
E^{DF}	– 8043.309653	– 8043.404857	– 8043.414155	– 8043.374896
ΔE^{Br}	6.511538	6.511115	6.510885	6.510788
$E^{DF} + \Delta E^{Br}$	– 8036.798115	– 8036.893742	– 8036.903270	– 8036.864108

For an explanation of used symbols, see footnote of Table II.

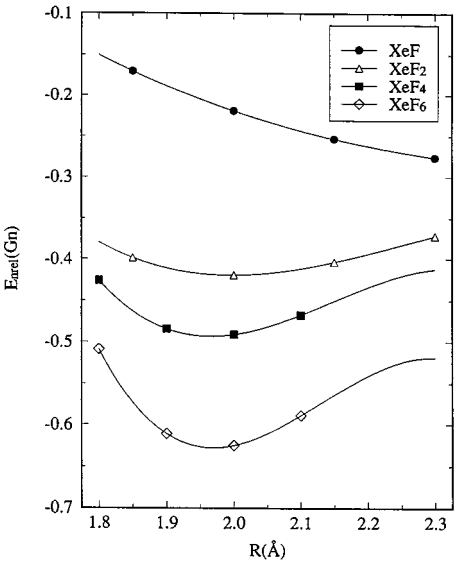


FIGURE 1. Nonrelativistic ground-state energy of XeF, XeF₂, XeF₄, and XeF₆ at various internuclear distances. Energies are shifted by 7331.1, 7430.3, 7628.9, and 7827.4 au, respectively.

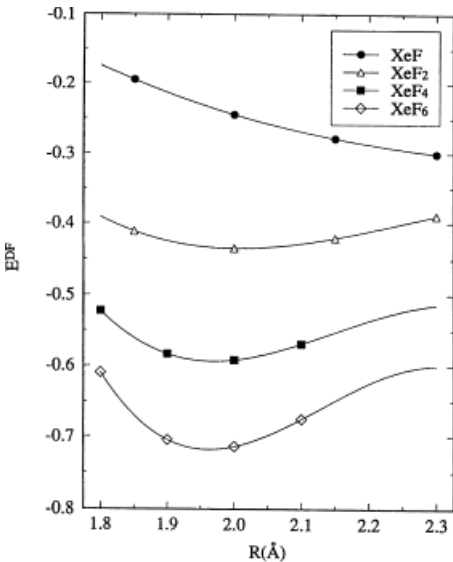


FIGURE 2. Dirac – Fock energy for XeF, XeF₂, XeF₄, and XeF₆ as a function of bond length. Energies are shifted by 7546.0, 7645.3, 7844.0, and 8042.7 au, respectively.

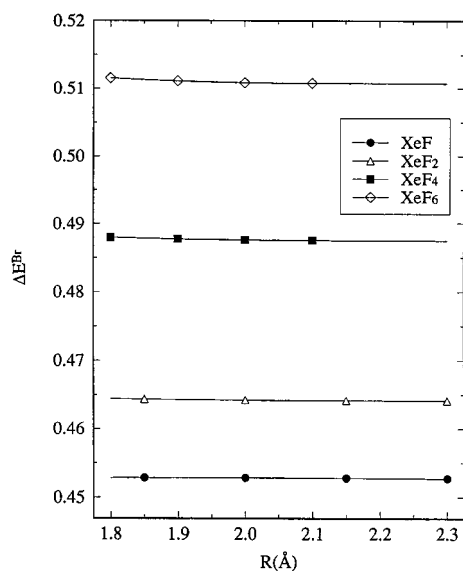


FIGURE 3. Magnetic part of the Breit correction as a function of internuclear distance Xe–F for the XeF, XeF₂, XeF₄, and XeF₆ molecules. All energies are shifted by –6 au.

bound only in the van der Waals sense. The potential energy curves for the ground state of the closed-shell molecule XeF₂, XeF₄, and XeF₆ have a minimum. The third-order polynomial fit of non-relativistic DF and DFB energies allows us to estimate for each molecule the minimum value of the energy (E_{\min}) and the corresponding Xe–F distance R_{\min} . These values are given in Table IV. Comparing these energies with the energies of Xe and F₂ one can see that the minimum values E_{\min} of xenon fluorides lie above the sum of corresponding energies of Xe and F₂, giving a negative value of the dissociation energy $D_e = E(\text{Xe}) + \frac{1}{2}nE_{\min}(\text{F}_2) - E_{\min}(\text{XeF}_n)$. Therefore the XeF_n molecules are predicted to be unbound in our HF, DF, and DFB calculations. This conclusion is not surprising, considering the small basis set employed and the neglect of correlation effects. We can conclude that the correlation effects are dominant for the proper prediction of dissociation energy of XeF_n and the relativistic effects are very small. The values of the dissociation energy for XeF_n ($n = 2, 4, 6$) are also given in Table IV. The role of the so-called correlation-relativity cross-term needs to be investigated. Further calculations that include both relativistic and correlation effects (using the relativistic CI program³⁶) are in progress. In the recent article of Crawford et al.²⁴ the corre-

TABLE IV. Minimum Value of Energy (E_{\min}) and Corresponding Xe–F Distance (R_{\min}).

Energy	R_{\min} (Å)	E_{\min} (au)	D_e (eV) ^a
XeF ₂			
$E^{\text{nrel}}(\text{Gn})$	1.9961	–7430.7196	–0.765
E^{DF}	2.0040	–7645.7353	–0.731
$E^{\text{DF}} + \Delta E^{\text{Br}}$	2.0044	–7639.2711	–0.721
Experiment ^b	1.977		2.78
XeF ₄			
$E^{\text{nrel}}(\text{Gn})$	1.9648	–7629.3931	–2.638
E^{DF}	1.9688	–7844.5938	–2.581
$E^{\text{DF}} + \Delta E^{\text{B4}}$	1.9691	–7838.1062	–2.558
Experiment ^c	1.95		5.69
XeF ₆			
$E^{\text{nrel}}(\text{Gn})$	1.9688	–7828.02764	–5.572
E^{DF}	1.9619	–8043.41837	–5.355
$E^{\text{DF}} + \Delta E^{\text{Br}}$	1.9622	–8036.90741	–5.317
Experiment ^{c, d}	1.89		8.40

Values obtained by the polynomial fit of results from Table III for XeF_n ($n = 2, 4, 6$). D_e is the calculated dissociation energy. For an explanation of used symbols, see footnote of Table II.

^a $D_e = E(\text{Xe}) + n/2E_{\min}(\text{F}_2) - E_{\min}(\text{XeF}_n)$.

^b V. I. Pepkin, Y. A. Lebedev, and A. Y. Apin, *Zh. Fiz. Khim.*, **43**, 1564 (1963); S. Reichman and F. Schreiner, *J. Chem. Phys.*, **51**, 2355 (1969).

^c Ref. 13.

^d Mean value taken from L. S. Bartell and R. M. Gavin, Jr., *J. Chem. Phys.*, **48**, 2466 (1968).

lation effects are included in the study of the structure of xenon hexafluoride; however, the dissociation energy is not discussed here.

The optimal Xe–F distances obtained in our DFB calculations for XeF₂, XeF₄, and XeF₆ are $R_{\min} = 2.00, 1.97$, and 1.96 Å, respectively. These values are 3, 2, and 7 pm bigger than the corresponding experimental values R_{exp} . The value of R_{exp} for xenon hexafluoride, quoted in Table IV, is the mean value derived by Bartell and Gavin from experimental data, while in the experimental geometry (C_{3v}) there are two Xe–F distances.²⁴ This may explain why the difference $R_{\min} - R_{\text{exp}}$ for XeF₆ is bigger than in the case of XeF₂ and XeF₄. The xenon fluorides are found to be unbound at the DF level of theory by about 0.73, 2.58, and 5.36 eV, respectively. It can be seen from Table IV that the inclusion of relativistic effects leads to a slight expansion in XeF₂ and XeF₄, while in XeF₆ it leads to a small contraction of the Xe–F distance. However, both effects are small (less than 0.5% of the bond length).

Conclusions

Relativistic effects are almost negligible for the proper prediction of the dissociation energy of xenon fluorides. DF calculations give Xe–F distances that are in good agreement with the corresponding experimental values. The number of scalar two-electron integrals, which is the main obstacle to the finite basis DF molecular calculations, can be significantly reduced by neglecting the small-valued $SS|SS$ and $SS|LL$ integrals.

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